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Docket No.
5475

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09/517426
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TO THE ASSISTANT COMMISSIONER FOR PATENTS

Transmitted herewith for filing under 35 U.S.C. 111 and 37 C.F.R. 1.53 is the patent application of:

Wilhelmina Helena Maria VELTMANS

For: PROCESS FOR THE PRODUCTION OF CRYSTALLINE ENERGETIC MATERIALS

Enclosed are:

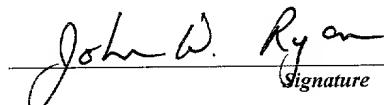
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 7 sheets of drawings.
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 Information Disclosure Statement
 Preliminary Amendment
 Other:

CLAIMS AS FILED

For	#Filed	#Allowed	#Extra	Rate	Fee
Total Claims	22	- 20 =	2	x \$18.00	\$36.00
Indep. Claims	4	- 3 =	1	x \$78.00	\$78.00
Multiple Dependent Claims (check if applicable)			<input type="checkbox"/>		\$0.00
				BASIC FEE	\$690.00
				TOTAL FILING FEE	\$804.00

A check in the amount of to cover the filing fee is enclosed.
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 Charge any additional filing fees required under 37 C.F.R. 1.16 and 1.17.
 Charge the issue fee set in 37 C.F.R. 1.18 at the mailing of the Notice of Allowance, pursuant to 37 C.F.R. 1.311(b).

Dated:


John W. Ryan
Signature

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Suite 300 South
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cc:

PATENT
Attorney Docket No. 5475.00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Wilhelmina Helena Maria VELTMANS

Serial No.: Unknown

Filed: Herewith

For: PROCESS FOR THE PRODUCTION OF CRYSTALLINE ENERGETIC MATERIALS

BOX: PATENT APPLICATION
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

PRELIMINARY AMENDMENT

Prior to the examination of the above application, please amend this application as follows:

IN THE CLAIMS:

Please delete claims 3-7, and insert therefor the following claims:

8. Process according to claim 1, wherein the crystallising mixture is transported continuously through the zone of ultrasonic vibration.

9. Process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz;

wherein the crystallising mixture is stirred during crystallisation;

wherein the crystallising mixture is transported continuously through the zone of ultrasonic vibration.

10. Process according to claim 9, wherein the temperature during recrystallization is between 15 and 75°C.

11. Process according to claim 1, wherein the temperature during recrystallization is between 15 and 75°C.

12. Process according to claim 2, wherein the temperature during recrystallization is between 15 and 75°C.

13. Process according to claim 10, wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

14. Process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz;

wherein the crystallising mixture is stirred during crystallisation;

wherein the crystallising mixture is transported continuously through the zone of ultrasonic vibration;

wherein the temperature during recrystallisation is between 15 and 75°C;

wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

15. Process according to claim 1, wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

16. Process according to claim 2, wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

17. Process according to claim 8, wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

18. Process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz;

wherein the crystallising mixture is stirred during crystallisation;

wherein the crystallising mixture is transported continuously through the zone of ultrasonic vibration;

wherein the temperature during recrystallisation is between 15 and 75°C;

wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

wherein the energetic materials are selected from the group of explosives and high energy oxidisers.

19. Process according to claim 18, wherein the energetic materials are selected from the group of explosives and high energy oxidisers.

20. Process according to claim 1, wherein the energetic materials are selected from the group of explosives and high energy oxidisers.

21. Process according to claim 2, wherein the energetic materials are selected from the group of explosives and high energy oxidisers.

22. Process according to claim 8, wherein the energetic materials are selected from the group of

explosives and high energy oxidisers.

23. Process according to claim 18, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, C120, ADN, AP, RDX, HMX and PETN.

24. Process according to claim 19, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, C120, ADN, AP, RDX, HMX and PETN.

25. Process according to claim 1, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, C120, ADN, AP, RDX, HMX and PETN.

26. Process according to claim 2, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, C120, ADN, AP, RDX, HMX and PETN.

27. Process according to claim 8, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, C120, ADN, AP, RDX, HMX and PETN.

PATENT
Attorney Docket No. 5475.00

REMARKS

The examiner is respectfully requested to consider this preliminary amendment prior to examination of the application. No new matter has been added.

Please grant any required extensions of time and charge any fees due in connection with this response to our deposit account no. 04-1425.

Respectfully submitted,

DORSEY & WHITNEY LLP.

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Dated: March 2, 2000

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Title: Process for the production of crystalline energetic materials

The invention is directed to a process for the production of crystalline energetic materials having improved stability and sensitivity properties.

Examples of energetic materials are energetic oxidisers and explosives. High energy oxidisers can be used as component in solid propellants for launchers and related applications. Examples of such oxidisers are hydrazinium nitroformate (HNF), nitramine hexaazaisowurtzitane (CL-20), ammonium dinitramide (ADN), ammonium-perchlorate (AP) and the like. Other materials falling in this class of energetic materials are explosives like cyclotrimethylene trinitramine (Hexogen, RDX), cyclotetramethylene tetranitramine (Octogen, HMX) and pentaerythrol tetranitrate (PETN).

These materials are all produced in a manner, wherein at some time during their preparation a crystallisation step occurs. Sometimes also a purifying recrystallisation step is included in the process. As the final product form of these materials is crystalline, one of the final steps of such a process includes a crystallisation.

For these crystalline energetic materials stability and sensitivity are very important parameters. Stability is of course important, as it determines the possible shelf life of the material during long term storage, and it further plays a role in the conditions under which the material can be stored and used (wider temperature range of storage and application conditions). More stable materials need less strict conditions for storage and use, or may be stored for a longer period of time under the same conditions.

The sensitivity, and more in particular the friction sensitivity and the impact sensitivity, are important, as it determines the care that should be taken during handling

and transport of the material. Also sensitivity determines to a large extent the governmental restrictions posed on transport and storage.

It is accordingly one object of the present
5 invention to improve the stability of crystalline energetic materials. It is another object of the invention to improve the sensitivity, such as impact and friction sensitivity thereof.

These and other objects are realised by the present
10 invention, which comprises a process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz. Preferably the
15 amplitude of an ultrasonic probe used for producing the vibration is between 0.4 and 30 μm .

The present invention is based on the surprising discovery, that by carrying out the last crystallisation step in the presence of ultrasonic vibration with a
20 frequency of between 10 and 100 kHz, the morphology, stability and sensitivity can be improved, i.e. the crystals become more rounded, the stability is better and the sensitivity is less.

In US patent No. 3,222,231 published on December 7,
25 1965, it is disclosed to improve the morphology of crystalline material, including ammonium perchlorate and hydrazinium nitroformate, by precipitating a solid solute out of solution, while mechanically agitating the solution and subjecting it to a high frequency vibration. According
30 to this patent, the processing under vibration improves the morphology of the crystals. The disclosure of this patent does not indicate anything about the effect of the treatment on stability and sensitivity.

According to a more preferred embodiment the present
35 invention is directed to an improvement in the production of hydrazinium nitroformate (HNF). HNF belongs to the class

of high energy oxidisers and can be used in high performance chlorine free solid propellants.

HNF is generally produced in crystalline form by combining hydrazine and nitroform under well defined conditions, followed by further purification using i.a. crystallisation. One method for the production of HNF is described in US patent number 5,557,015. According to this method HNF is prepared in very pure form by reacting hydrazine and nitroform in a system that is a solvent for nitroform and a non-solvent for hydrazinium nitroformate, in the presence of a proton transferring medium.

The stability of the present energetic materials, and more in particular of HNF, can be determined by vacuum thermal stability (VTS) in accordance with STANAG 4479 at 15 60 and 80°C for 48 to 100 hours.

The friction sensitivity is determined by BAM friction in accordance with ONU 3b)i), the impact sensitivity by BAM impact in accordance with ONU 3a)ii).

It has been noted that whereas the HNF crystals are 20 having an aspect ratio of more than 4 after crystallisation without ultrasonic vibration, the crystals produced in accordance with the process of the present invention have an aspect ratio, which is sometimes lower than this, depending both on the applied amplitude of the ultrasonic 25 probe and the recrystallisation method used. However, it has also been found that there is no direct link between the aspect ratio of the crystals on the one hand and the stability or sensitivity on the other hand.

The process of the present invention can be carried 30 out in various ways. In general it is important that during crystallisation the crystallising mixture is subjected to treatment with the ultrasonic vibration. This process can be applied during crystallisation and during recrystallisation.

35 In case of batch processing one may subject the whole batch at the same time to an ultrasonic vibration. In

the alternative it can be done by stirring the crystallising mixture in such a way that the batch content moves through a region of ultrasonic vibration sufficiently frequently to obtain the effect. This can for example be 5 done by using an ultrasonic probe, whereby the stirring regime or the construction of the crystalliser is such that the suspension passes the vibration zone frequently. It is also possible to include the treatment in a recirculation loop of the crystalliser.

10 The temperature of the treatment is not critical, although it may have some effect on the actual stability, sensitivity and morphology. Temperatures between 0 and 100°C, preferably between 15 and 75°C can be used.

15 The present invention is now explained on the basis of the production of crystalline HNF, although it will be clear to the skilled person that other materials may be produced using the same principles, wherein variation may be applied, if necessary to take into account the actual 20 production methods of other materials, while maintaining the basic principles of the invention.

In the operation of the present invention first HNF is prepared from hydrazine and nitroform, for example as disclosed in the cited US patent No. 5.557.015, The contents of which is incorporated herein by way of 25 reference. In general this means that nitroform having a purity of more than 98.5 %, dissolved in dichloroethane, and water (6 vol.%) are mixed. At 0°C an equimolar amount of hydrazine, purity 99.5%, is added and the mixture is stirred, while keeping the temperature between 0 and 5°C. 30 The crystalline HNF obtained thereby is then subjected, either in the reaction mixture, or after crystallisation and/or additional purification, to a final (re)crystallisation in the presence of the ultrasonic vibration.

35 The invention is now further explained on the basis of a number of examples.

EXAMPLE 1 (ultrasound (US) applied during cooling-crystallisation of HNF)

5 Nitroform, dissolved in dichloroethane (23 wt.-% nitroform), and water (6 vol.-%) are mixed. At 0°C an equimolar amount of hydrazine, purity 99.5%, is added and the mixture is stirred, while keeping the temperature between 0 and 5°C. The crystalline HNF obtained thereby is
10 separated from the mother liquor and redissolved in methanol.

The HNF solution in methanol is subsequently cooled yielding HNF crystals. This experiment has been performed in the absence of ultrasound (US) (reference, amplitude 15 0 μm) and under ultrasonic vibration with a frequency of 20 kHz and varying ultrasonic amplitude. Figures 1, 2, 3 and 4 show the properties of HNF crystals obtained in several experiments in which the amplitude of ultrasonic vibration is varied during cooling crystallisation.

20 Figure 1 shows the positive effect of ultrasound (US) on the morphology of HNF, expressed as the Length over Diameter (L/D) and average particle size ($X_{\text{sph.}}$).

Figure 2 shows the positive effect of ultrasound (US) on the sensitivity of HNF, expressed in BAM impact and 25 BAM friction values ([N] and [N.m] respectively).

Figure 3 shows that ultrasound (US) has a positive effect on the thermal stability of HNF at 60°C. The initial gas evolution decreases in comparison to the reference sample (no ultrasound (US) = amplitude of 0 μm) and the gas 30 evolution in time decreases as well when a low amplitude of 0.4 μm is applied.

Figure 4 gives an indication of the positive effect of ultrasound (US) on thermal stability at 80°C. At 80°C the effect becomes more apparent (on the larger gas 35 evolution scale) after -80 hrs. These four figures clearly show the positive effect of ultrasound (US) during cooling

crystallisation on morphology, sensitivity and stability in comparison to the reference HNF crystallised in absence of ultrasound (US).

5 **EXAMPLE 2 (ultrasound (US) applied during drowning out crystallisation of HNF)**

HNF is prepared by the method described in example 1. The HNF in methanol solution is subsequently closed in a 10 methylene chloride/methanol solution yielding HNF crystals. This experiment has been performed in the absence of ultrasound (US) (reference, amplitude 0 μm) and under ultrasonic vibration with a frequency of 20 kHz and varying ultrasonic amplitude. Figures 5, 6 and 7 show the properties 15 of HNF crystals obtained in several experiments in which the amplitude of ultrasonic vibration is varied during drowning out crystallisation.

Figure 5 shows the negative effect of ultrasound (US) on morphology; L/D increases which implies that the 20 HNF crystals are more needle shaped.

Figures 6 and 7 show VTS results at 60 and 80°C, respectively.

From figure 6 it can be clearly seen that ultrasound (US) application reduces initial gas evolution with a 25 minimum initial gas evolution at a low to medium ultrasound (US) amplitude (0.4-2 μm).

Figure 7 shows that at higher temperature (80°C) the application of ultrasound (US) not only reduces the initial gas evolution but also the overall gas evolution rate in 30 time. These three figures clearly show that in spite of the negative influence of ultrasound (US) during drowning-out crystallisation on morphology, ultrasound (US) has a positive influence on stability in comparison to the reference HNF crystallised in absence of ultrasound (US).

Claims

1. Process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz.
5
2. Process according to claim 1, wherein the crystallising mixture is stirred during crystallisation.
3. Process according to claim 1 or 2, wherein the crystallising mixture is transported continuously through the zone of ultrasonic vibration.
10
4. Process according to claims 1-3, wherein the temperature during recrystallisation is between 15 and 75°C.
5. Process according to claims 1-4, wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 30 μm .
15
6. Process according to claims 1-5, wherein the energetic materials are selected from the group of explosives and high energy oxidisers.
7. Process according to claim 6, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, Cl_2O , ADN, AP, RDX, HMX and PETN.
20

ABSTRACT

The invention is directed to a process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz.

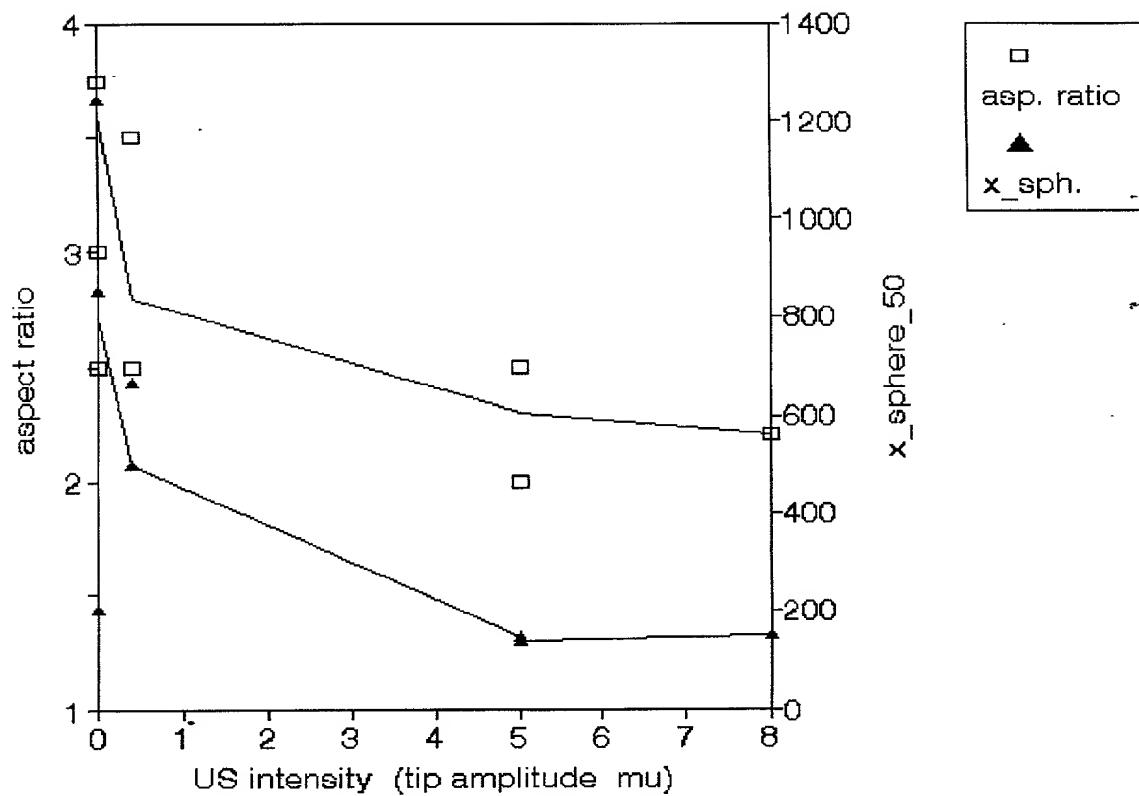


Figure 1

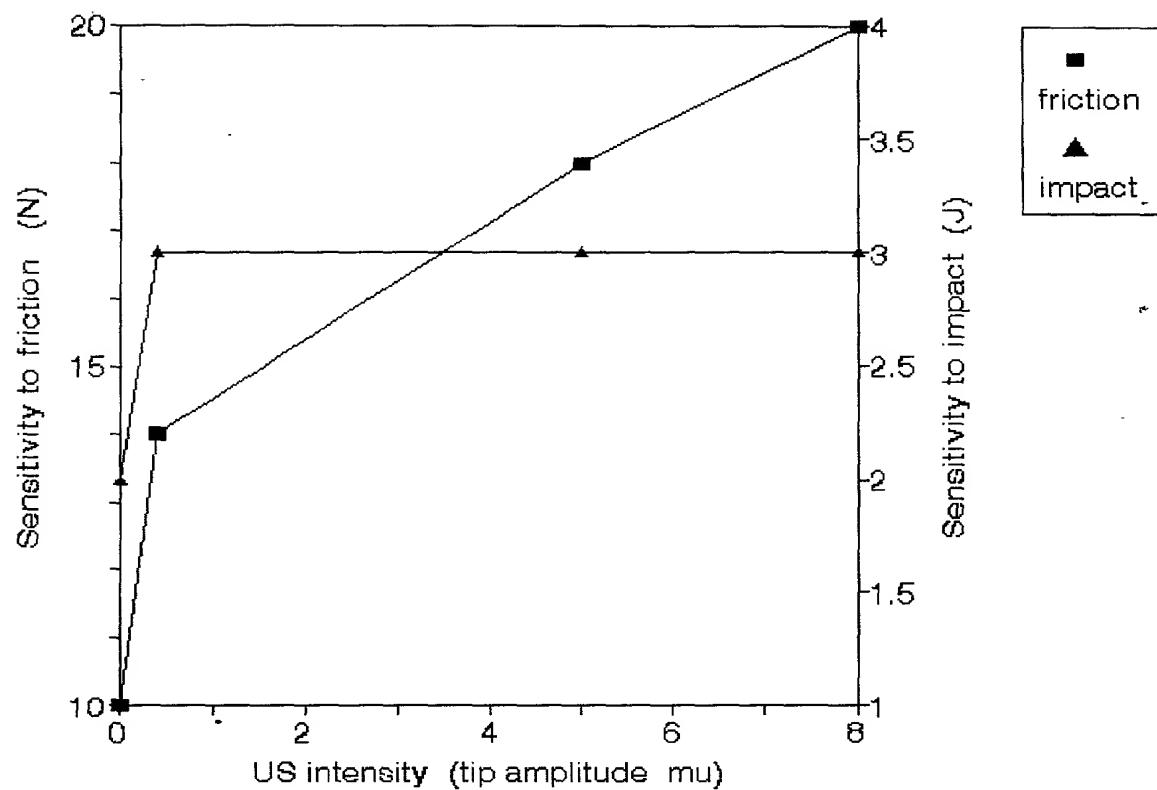


Figure 2

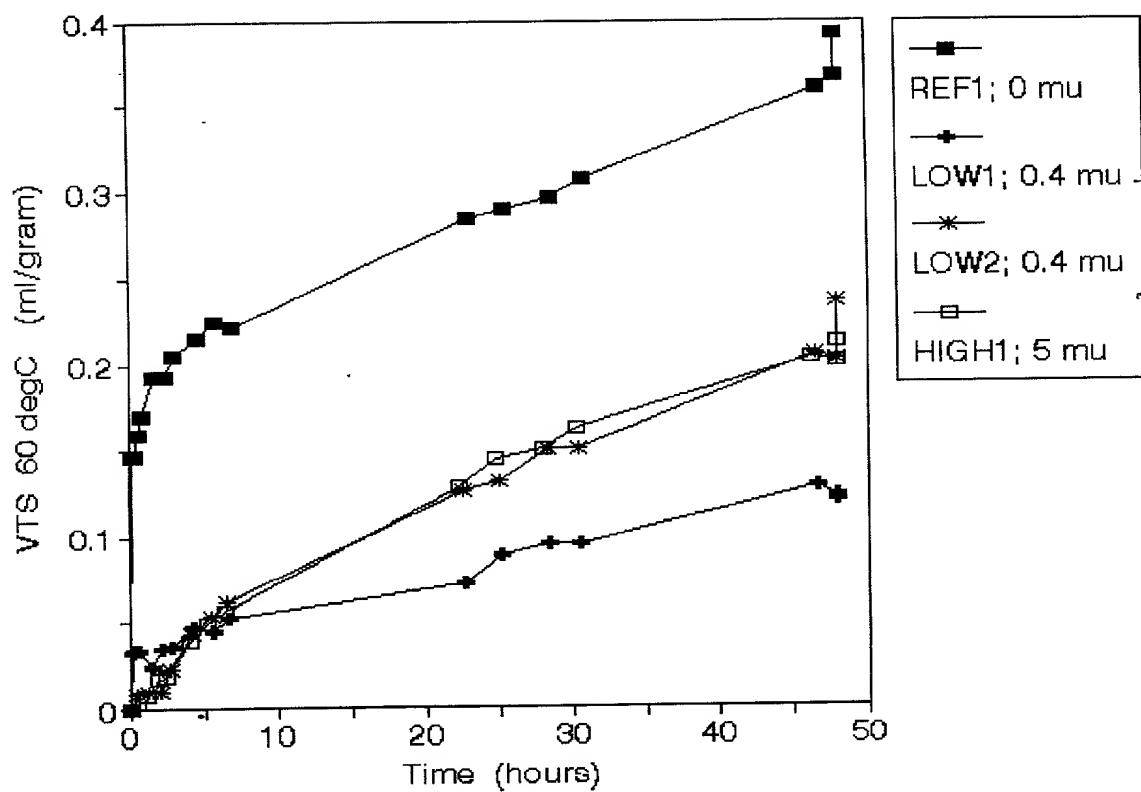


Figure 3

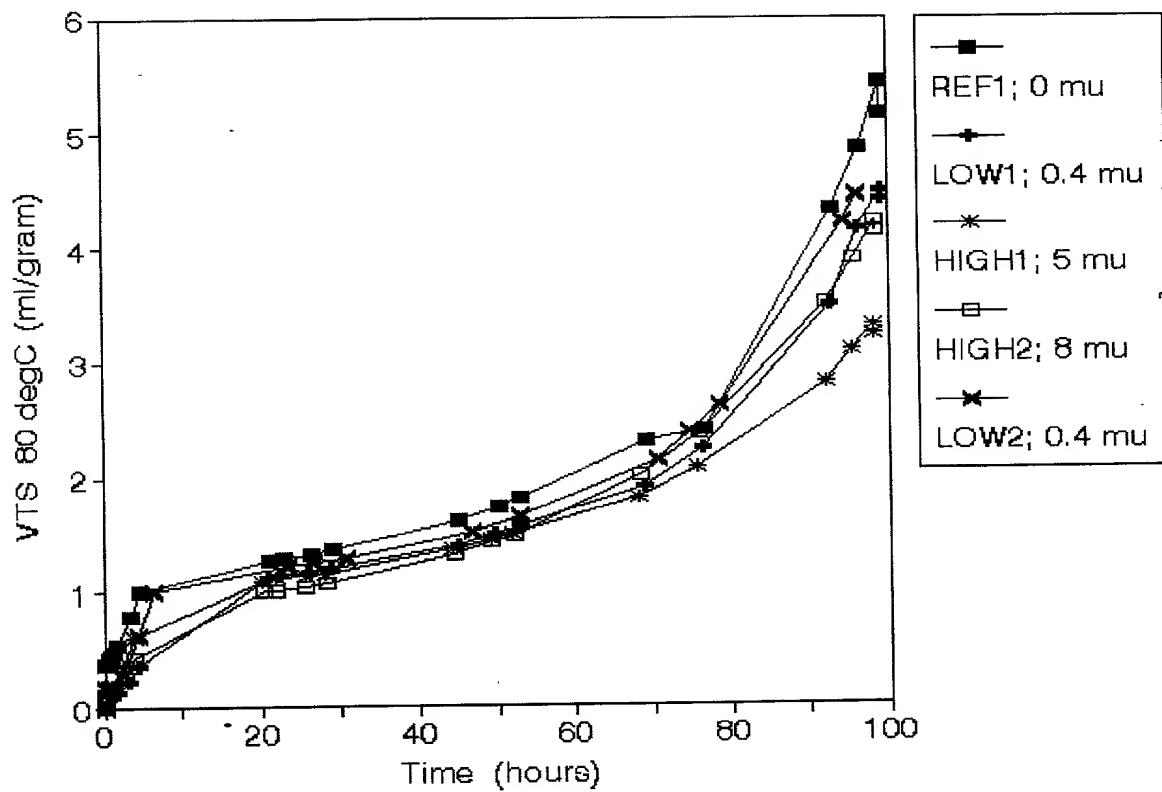


Figure 4

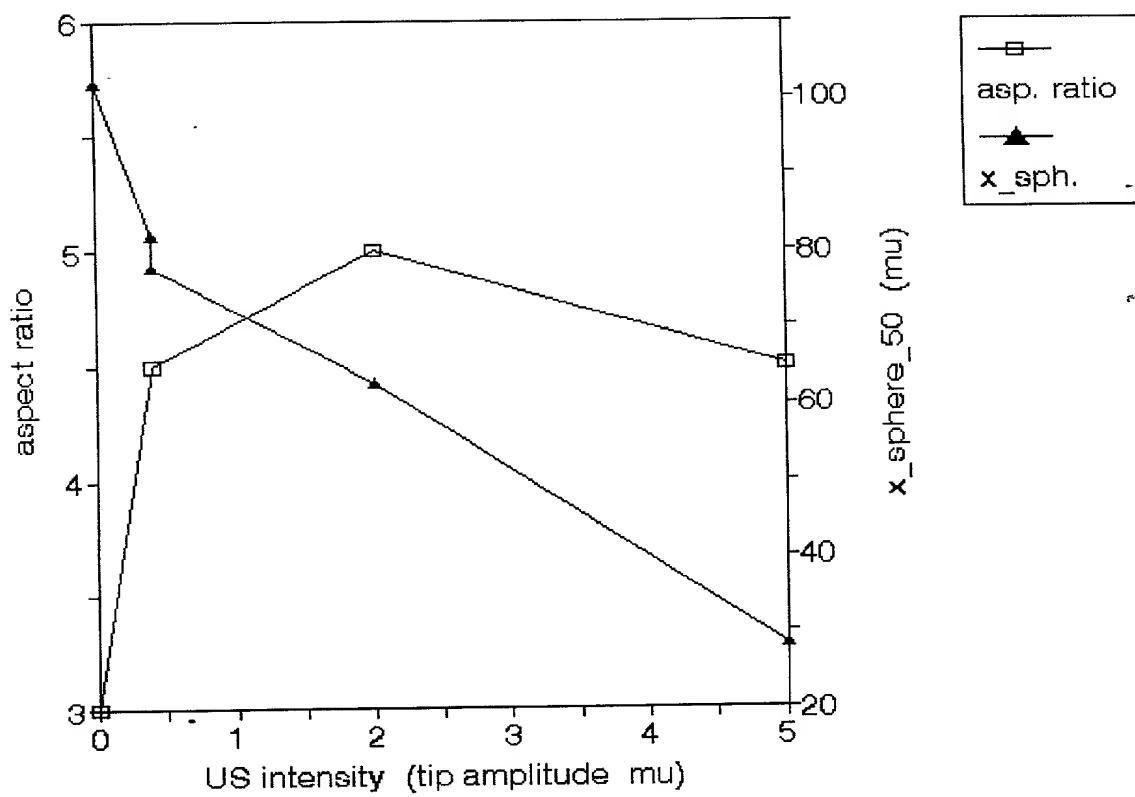


Figure 5

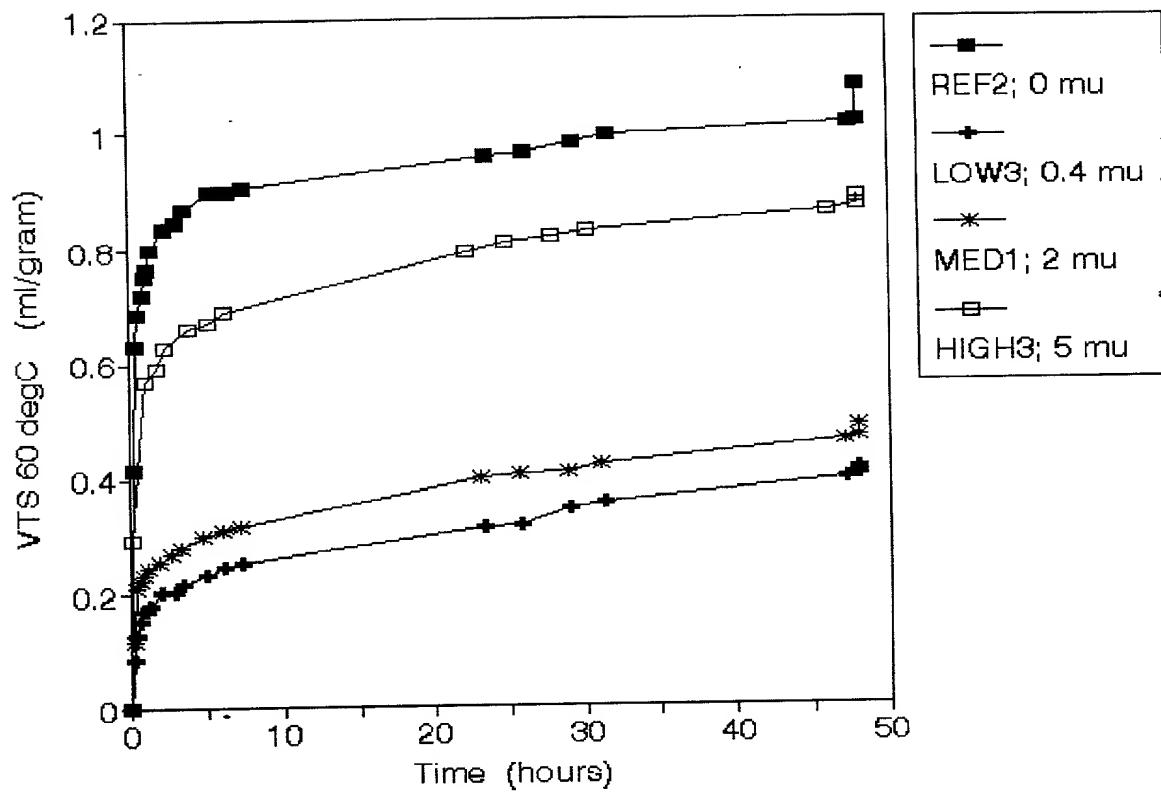


Figure 6

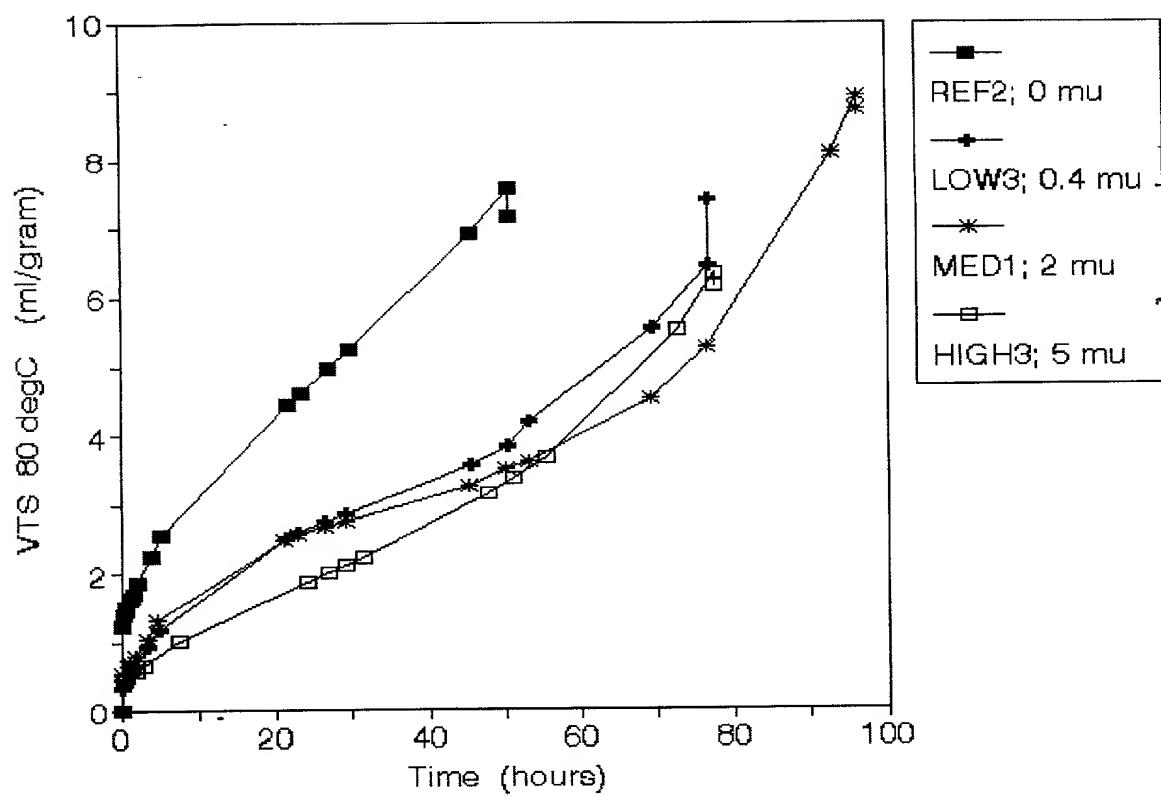


Figure 7